

Attorney Docket No. 13631-46

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NOV 21 2006**Remarks

This application has been reviewed in light of the Office Action dated July 21, 2006. In view of this amendment, Claims 18 and 44-52 are now pending in this case, with Claims 18, 47 and 52 in independent form.

Claims 18 and 47 are amended to call for a product and bonded structure, respectively, comprising a reacted multilayer foil having a heat of formation more negative than -30kJ/mol-atom. Support for this amendment may be found in the application as published (U.S. Patent Publication No. 2004/0247931) at least at paragraph [0022] and the article by T. P. Weihs titled "Self-Propagating Reactions in Multilayer Materials," *Handbook of Thin Film Process Technology*, 1997, (herein the "Weihs article"), incorporated by reference in its entirety in the present application. Applicants respectfully submit that no new matter is added by this amendment.

Claim 51 is new and is directed to a bonded structure comprising a joining region having "an array of openings." Support for Claim 51 may be found in the application as published at least at paragraphs [0008], [0046]-[0049], and Figure 4. Applicants respectfully submit that no new matter is added by this amendment.

Claim 52 is new and is directed to a bonded structure comprising a joining region including a compound having a heat of formation more negative than -30kJ/mol-atom and a joining material. Support for Claim 52 may be found in the application as published at least at paragraphs [0022], [0035], and [0036]. Applicants respectfully submit that no new matter is added by this amendment.

The Provisional Obviousness-Type Double Patenting Rejections

In the Office Action, Claims 18 and 44-50 stand provisionally rejected under obviousness-type double patenting over co-pending U.S. Patent Application No. 10/761, 444. In

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addition, Claims 18 and 44 stand provisionally rejected under obviousness-type double patenting over co-pending U.S. Patent Application Nos. 10/976,877 and 10/898,650. Because these rejections are provisional in nature, the Applicants wish to defer action in this regard until the provisional status of the rejections is removed. As such, upon indication of allowable subject matter in this or the related applications, the Applicants will file the appropriate terminal disclaimer to obviate the rejection.

The 35 U.S.C. §102(b) Rejection of Claims 18, and 44-50

In the Office Action, Claims 18 and 44-50 stand rejected under 35 U.S.C. §102(b) as anticipated by U.S. Patent No. 5,251,803 (herein "Kashiba"). It is well-established that for a reference to defeat a claim's novelty under 35 U.S.C. § 102 (i.e., anticipate the claim), it must disclose each and every element of the claim. Advance Display Sys. v. Kent State Univ., 212 F.3d 1272 (Fed. Cir. 2000).

In the Office Action, the Examiner states that Kashiba discloses a first body 2C bonded to a second body 1, wherein said bodies are bonded together by a reactive multilayer foil 2a, 21 that is disposed between said bodies and ignited (Figures 8a, 8b, columns 12-13). At the outset, the Applicants respectfully point out that as clearly shown in Figure 8b of Kashiba, the body 2C is not bonded to second body 1.

Claims 18 and 47 of the present application are amended to call for a product or bonded structure comprising a reacted multilayer foil having a heat of formation more negative than -30kJ/mol-atom. Support for this amendment may be found in paragraph [0022] of the present application which provides that the multilayer foil reacts "to form compounds with large negative heats of formation... as described in T. P. Weihs, "Self-Propagating Reactions in Multilayer Materials," *Handbook of Thin Film Process Technology*, 1997, which is incorporated

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herein by reference in its entirety." The Weihs article, incorporated by reference in this application and attached hereto as Appendix A, describes that the reacted multilayer foil has an enthalpy, or heat of formation, more negative (i.e., greater) than -30 kJ/mol. (see Section F7.1, paragraph 3). One having ordinary skill in the art will appreciate that the negative sign associated with the heat of formation indicates exothermicity and that a larger negative number is often said to be greater (in magnitude) than a smaller negative number.

In contrast, Kasuba describes the use of a combination of titanium/zirconium/silver (i.e., the thin film layer 21) and copper (i.e., copper members 2A, 2B, and 2C) to create a low-melting-point liquid (880°C minimum) (e.g., the molten layer described in column 14, at lines 31-34) that must finally solidify into at least one of several compounds, none of which exhibit a heat of formation more negative than -30 kJ/mol. One having ordinary skill in the art will appreciate that the heats of formation of compounds of copper and active metals (Ti, Zr, Hf) are as follows (see e.g., Boer et al, "Cohesion in Metals: Transition Metal Alloys," North-Holland, Amsterdam, 1988):

Compound	Heat of formation, kJ/mol-atom
TiCu ₄	-23
TiCu	-9.6
Ti ₂ Cu	-26
ZrCu ₃	-14
Zr ₂ Cu ₃	-12
ZrCu	-24
Zr ₂ Cu	-17
HfCu ₄	-14
Hf ₂ Cu ₃	-13
Hf ₂ Cu	-15

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Further, one having ordinary skill in the art will appreciate that silver, mentioned in Kashiba at col. 15, line 28, forms no compounds with copper.

As illustrated above, Kashiba fails to describe a product or joint comprising a reacted multilayer foil having a heat of formation more negative than -30kJ/mol-atom, as called for in independent Claims 18, 47, and 52. Accordingly, because Kashiba et al. fails to disclose each and every element of independent Claims 18, 47, and 52, Applicants respectfully request that the §102(b) rejection be withdrawn.

In view of the above remarks and amendments, Applicants respectfully submit that Claims 18 and 44-51 are in condition for allowance. Favorable consideration in this regard is earnestly solicited.

No fee is believed due for entry of this Response, however, if any fee is deemed necessary, the Commissioner is authorized to charge any fees related to the entry of this Reply to Deposit Account Number 501358.

Applicants' undersigned attorney may be reached by telephone at (973) 597-2500. All correspondence should continue to be directed to our address listed below.

Respectfully submitted,



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APPENDIX A

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Self-Propagating Reactions in Multilayer Materials

F7 Self-Propagating Reactions in Multilayer Materials

Timothy P Weihs

F7.0 INTRODUCTION

This chapter explores exothermic formation reactions that propagate rapidly through multilayer materials with a burst of heat and light. The multilayer samples consist of many nanoscale layers that are chemically distinct and typically alternate between a transition metal such as Ti or Ni and a light element such as B or Al. These pairs of elements are chosen because they react to form stable compounds with large, negative heats of formation and high adiabatic reaction temperatures. One starts the formation reactions by applying a pulse of energy to the edge of a sample. The energy enables atomic mixing in the local vicinity, which leads to the formation of a compound and the release of heat. The heat diffuses into the remainder of the sample and initiates the same reaction in adjoining volumes. With sufficiently large and rapid heat generation, the reaction becomes self-sustaining and propagates across the whole sample at speeds ranging from 0.1 to 25 m s⁻¹. Since the reactions do not require additional atoms from their surrounding environments (such as oxygen in the case of combustion), they are self-contained sources of energy. They can produce heat rapidly and locally, and therefore have unique commercial applications as heat sources for joining and ignition. Currently, however, there is only limited knowledge of how these materials react. Fewer than ten material systems have been investigated, and many scientific questions remain regarding their properties and transformations. This chapter reviews the experimental and theoretical investigations that have been performed to date and summarizes the current understanding.

F7.1 BACKGROUND

Many simple, self-contained reactions can generate heat fast enough to be self-sustaining. Common examples are explosive crystallization of amorphous films [1-5], thermite reduction reactions of metals and oxides [6-8], and compound formation reactions in powder samples [9-11]. In each of these examples the reactants, as a system, are in a metastable state with significant excess energy. If a point within a sample is perturbed with energy, the local reactants transform into a stable state and release heat into the remainder of the sample. If this heat is released rapidly enough, its diffusion sustains the transformation and the reaction propagates throughout the whole sample without additional inputs [1-11].

In the early 1980s Russian scientists reported self-sustaining reactions in powder compacts [10]. They found that the formation of TiB₂ from Ti and B powders could produce heat fast enough to propagate as a 'white solid flame' across a powder compact. This discovery spawned a whole new field of research into a processing method called Self-Propagating, High-Temperature Synthesis (SHS) [9-11]. This method uses self-sustaining, formation reactions in powder compacts to join materials and produce hard compounds in near-net shapes [6-11]. Table F7.1 lists a number of exothermic formation reactions, some of which are used in SHS processing [12-14]. Note that when the compounds form adiabatically, their reaction temperatures are very high and many reach a state where they are at least partially liquid.

With the advent of modern thin film deposition techniques, scientists and engineers can now fabricate fully dense multilayer materials [15] with similar exothermic reactions [16-26]. The samples have many nanoscale layers that are chemically distinct and typically alternate between a transition metal and a light element. Since the layers are only nanometers thick, diffusion distances are very short and atoms can mix

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Self-Propagating Reactions in Multilayer Materials

Table F7.1. Thermodynamic data for selected formation reactions [12-14]

Reaction	Heat of reaction (kJ mol ⁻¹)	Adiabatic reaction temperature (°C)	Phase of reaction product
Ti + 2B → TiB ₂	-108	2828	solid & liquid
Zr + 2B → ZrB ₂	-108	3000	solid & liquid
Hf + 2B → HfB ₂	-110	3376	solid & liquid
V + 2B → VB ₂	-68	2291	solid
Nb + 2B → NbB ₂	-72	2282	solid
Ta + 2B → TaB ₂	-63	2400	solid
Ti + C → TiC	-93	3067	solid & liquid
Zr + C → ZrC	-104	3417	solid & liquid
Hf + C → HfC	-105	3830	solid & liquid
V + C → VC	-30	1957	solid
Nb + C → NbC	-69	2698	solid
Ta + C → TaC	-72	2831	solid
5Ti + 3Si → Ti ₅ Si ₃	-72	2120	solid & liquid
5Zr + 3Si → Zr ₅ Si ₃	-72	2250	solid & liquid
5Hf + 3Si → Hf ₅ Si ₃	-70	2200	solid & liquid
5V + 3Si → V ₅ Si ₃	-58	1519	solid
5Nb + 3Si → Nb ₅ Si ₃	-57	2060	solid
5Ta + 3Si → Ta ₅ Si ₃	-42	1547	solid
2Nb + Si → Nb ₂ Si	-45	1306	solid & liquid
Ti + Al → TiAl	-36	1227	solid
Zr + Al → ZrAl	-45	1480	solid & liquid
Hf + Al → HfAl	-46		
Ni + Al → NiAl	-59	1639	solid & liquid
Pd + Al → PdAl	-92	2380	liquid
Pt + Al → PtAl	-100	2800	liquid

be self-propagating in a multilayer film with nanoscale layers. So far, self-sustaining reactions have been reported in TiB [23], NbSi [20], ZrSi [17], RuSi [16], Ni/Al [18, 19, 22, 25], Monel(7Ni-3Cu)/Al [24, 25], Ti/Al [24], and Pd/Al [21] multilayer materials. Reactions in these systems have been driven by formation enthalpies (ΔH_f) that are equal to or greater than -36 kJ mol^{-1} . Based on these results, and based on the inability to ignite the formation of CrSi₂ ($\Delta H_f = -27 \text{ kJ mol}^{-1}$) in Cr/Si multilayers [27], we conjecture that a formation reaction must generate an enthalpy greater than -30 kJ mol^{-1} to self-propagate in a multilayer sample.

The basic driving force for self-propagating formation reactions is a reduction in atomic bond energy. Consider the cross-sectional view of a binary multilayer foil in Figure F7.1. When the left end of the foil is pulsed with a spark, the local atoms diffuse normal to the layers with A-A and B-B bonds being exchanged for A-B bonds. This bond exchange generates heat which is then conducted along the foil and facilitates more atomic mixing. The reaction quickly becomes self-sustaining and travels down the foil in a volume termed the reaction zone. Simple formation reactions can travel as fast as 25 m s^{-1} [20, 24-26]; they can reach temperatures above 1500°C [20, 22, 24], and they can emit bursts of heat and light very rapidly [16-25, 28]. This chapter addresses the fabrication, the characterization, and the properties of these exothermic formation reactions.

F7.2 FABRICATION OF MULTILAYER FOILS

Reactive multilayer materials are most commonly fabricated using physical vapour deposition [15, 29], and occasionally via mechanical techniques such as repeated rolling of layered composites [21]. Methods of physical vapour deposition are reviewed in detail elsewhere in this handbook and therefore will not be discussed here. However, a few important aspects of depositing reactive multilayer foils will be noted.

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Self-Propagating Reactions in Multilayer Materials

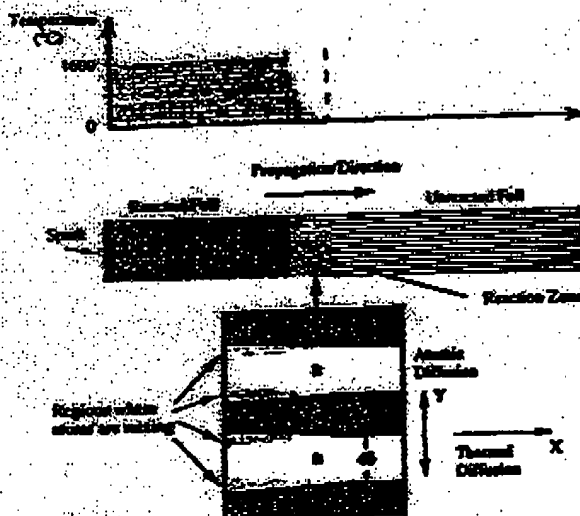


Figure F7.1. Cross-sectional view of atomic and thermal diffusion during a self-propagating, exothermic formation reaction in an A/B multilayer sample.

First, and most importantly, there is the need to generate the chemically distinct layers that are shown in figure F7.1. One common method is to deposit material in a codeposition geometry. In this method both sources are directed onto one substrate and the atomic fluxes from each source are shuttered to deposit the alternate layer. A second method is to eliminate shuttering altogether and simply rotate substrates over two sources which have physically distinct atomic fluxes. In this method each pass over a source generates an individual layer. Both methods have been used to produce reactive multilayer films and foils. A second important factor in fabrication is the degree of atomic intermixing that occurs during deposition. While the individual layers are designed to be chemically distinct, the energy of the arriving atoms and the thermal energy of the substrate can lead to atomic mixing between the layers during deposition. Subsequent sections of this chapter show that this intermixing degrades the self-propagating reactions and can be minimized by depositing the multilayers onto cooled substrates, particularly when multilayers are sputter deposited.

Most of the reactive multilayers tested to date have been deposited onto uncooled substrates such as Si, glass, or photoresist [16, 17, 19, 20, 22-25]. The samples have nanoscale layering (1 to 1000 nm thick), and it is likely that each of these samples have some intermixing between the individual layers. The total thicknesses of the multilayers vary from 1 μm for thin films that were deposited and tested on their substrates to 100 μm for thick foils that were stripped from their substrates and tested as free-standing samples. In general, the thick, free-standing foils are easier to characterize than the thin films because they can be handled like "bulk" samples [24, 25].

F7.3 PROPERTIES OF REACTIVE MULTILAYER FOILS

F7.3.1 As-Deposited Microstructures and Chemical Profiles

Reactive multilayer films and foils often contain some combination of crystalline and amorphous layering following their deposition. The alternate layers in metal/metal systems such as the aluminides in table F7.1 are typically polycrystalline. The layers have standard growth textures and the in-plane grain size tends to scale with layer thickness. However, an intermixed layer often forms between the two polycrystalline layers. An example for an Al/Zr multilayer foil is seen in figure F7.2. The cross-sectional bright field image clearly illustrates the polycrystalline layers of Al and Zr and an apparently amorphous intermixed

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Self-Propagating Reactions in Multilayer Materials

layers have been observed in other immiscible multilayers where the alternating metals have large, negative heats of mixing [30-33]. For the boride, carbide, and silicide systems in table F7.1, the layering is quite different. The metallic layers are still polycrystalline, but the B, C or Si layers are normally amorphous due to the low deposition temperatures [34]. This is important because it adds the heat of crystallization to the reaction [20]. For example, when amorphous Si reacts with a transition metal to form a crystalline silicide, its heat of crystallization ($-14.2 \text{ kJ mol}^{-1}$) will increase the heat of formation beyond the values listed in table F7.1. The disordered structure of the as-deposited B, C and Si is also likely to impact atomic diffusion within these layers, and therefore should be considered [35].

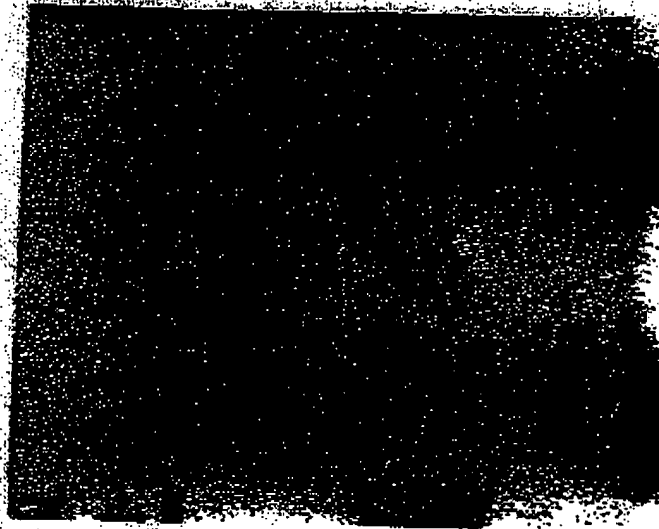


Figure F7.2. Cross-sectional TEM micrograph of an Al/Zr multilayer. The light layers are Al and the dark layers are Zr [36]. Note the intermixed zone between each Al and Zr layer.

Besides atomic structure, the chemical profile of the individual layers can also impact reaction properties. Two concerns are considered. The first is the degree of intermixing that occurs between layers during deposition. Intermixing (and the corresponding exchange of A-A and B-B bonds for A-B bonds) reduces the chemical energy that is stored within each sample. The thicker the intermixed layer, and the more extensive the bond exchange, the larger the energy loss [24-26]. Figure F7.3 shows a cross-sectional mapping of Al in as-deposited Al/NiAl multilayers that was obtained using parallel electron energy loss spectroscopy (PEELS) [36]. While this image yields only a qualitative distribution of Al (shown in white), it is possible to estimate the thickness of an average intermixed layer (3 nm) [24-26, 36]. From this thickness one can approximate a loss of chemical bond energy during deposition. A second concern regarding chemical profiles is the sharpness of the profile at the interface between the layers. The sharpness of the profile should be determined in large part by the phases that form within the intermixed region between the layers. The formation of a compositionally invariant phase, such as a line compound, could produce a very sharp profile. The formation of a solid solution [31] or a compound with a variable chemistry [37] could produce a smooth profile. Evidence of this second type of profile was reported by Ma *et al* [31]. They found that composition varied gradually across interfaces in Ni/Al multilayers with a Ni₃Al composition, as shown in figure F7.3(b). While their large probe size (4 nm) may have smoothed the actual profile, a gradual variation of composition is possible in such a multilayer and it will impact the rate of diffusional mixing. Generally, smooth chemical profiles will tend to decrease atomic fluxes between layers compared to sharp profiles and are likely to lead to lower reaction velocities.

F7.3.2 The Ignition and Velocities of Self-Propagating Reactions

Researchers have employed several different means for igniting self-propagating reactions in nanoscale multilayers. Generally, the reactions are started by polishing one end of a sample with a small burst of

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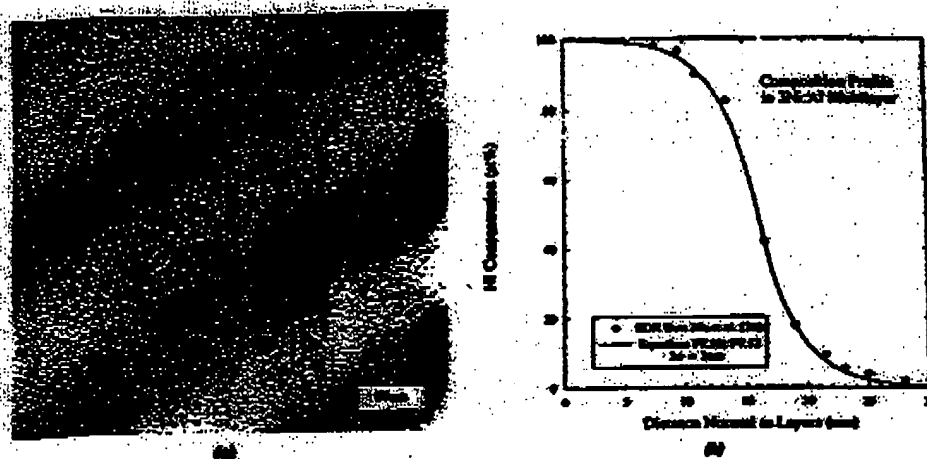


Figure F7.1. (a) A cross-sectional FEELS mapping of Al in a Monel/Al multilayer foil [31]. The light layers are Al. (b) Composition profile through the thickness of a Ni/Al multilayer with a Ni₃Al composition [31]. Equations (F.11) and (F.12) are fit to the data with $2m = 3$ nm.

energy. The energy can be applied using the impact from a sharp stylus [16, 17, 20], a spark from an electrical source [16, 17, 19, 21, 23-25], the heat from a filament [18, 22], or the radiation from a laser [20]. The minimum power required to ignite a particular reaction has not yet been quantified, but two studies suggest some dependences. Ma *et al* [19] investigated the effect of multilayer period on ignition using Ni/Al multilayers. Their results suggest that films with larger periods require more power than films with smaller periods, as one might expect. They also found that raising the initial sample temperature decreased the power required to ignite a given sample. Wickersham and Poole [17] conducted a similar study on Zr/Si films with a given multilayer period and found that thicker films were ignited at lower sample temperatures than thinner films.

Once formation reactions are ignited, the speeds at which they propagated can be characterized using photodiodes [24, 25, 38] or high-speed cameras [19, 20, 22]. A schematic of a photodiode and a simple optical system used by Ricks *et al* [38] is shown in figure F7.4. A free-standing reactive foil is clamped flat on a Cu plate, and the exothermic reaction is started at one end of the foil using an electric spark from a battery and two point probes. A microscope with a long focal length generates an image as the reaction propagates up the foil, and a Si photo diode records its passage. Voltage signals are recorded on an oscilloscope as the reaction passes, and the time between voltage steps and the distance between steps determines the velocity of the reaction [38]. Researchers have also captured reaction fronts traversing a sample using high-speed cameras. Cleveger *et al* [20] and Dyer *et al* [22] used a sequence of photographs to measure reaction velocities for Ni/Si and Ni/Al multilayers; their results are shown along with velocities for other samples in figure F7.5(b).

Figures F7.5(a) and (b) show that the velocity of a self-propagating reaction is a strong function of multilayer period. As period decreases, the diffusion distances are smaller and atoms can mix more rapidly. Heat is released at a higher rate, and reactions travel faster through a sample. This dependence is intuitively expected based on our knowledge of one-dimensional atomic diffusion. The more novel dependence is the sharp drop in velocity for the Monel/Al data sets below a critical period. The source of this sharp drop-off in the Monel/Al samples (and its absence in the two large Ni/Al data sets) is explored in the next two sections by considering the heats and the transformations of each formation reaction.

F7.3.3 Heat Losses due to Atomic Interdiffusion during Deposition

When a multilayer sample reacts to form a compound, we define the reduction in atomic bond

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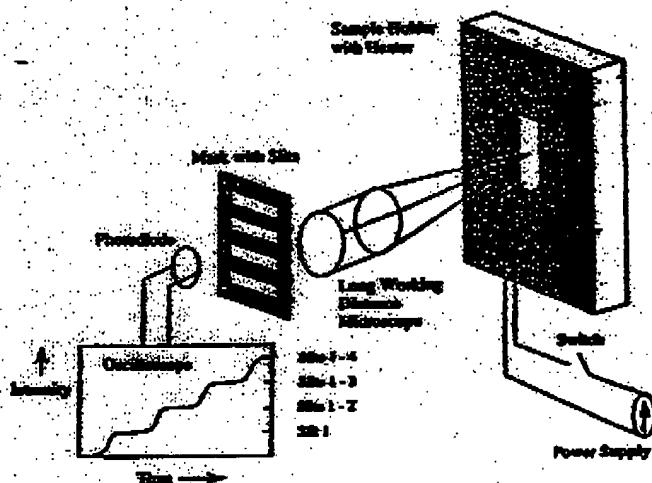


Figure F7.4. Schematic diagram showing the measurement of reaction velocities [38]. The reaction is started with a small spark and its passage is recorded using a photodiode, a mask and an oscilloscope.

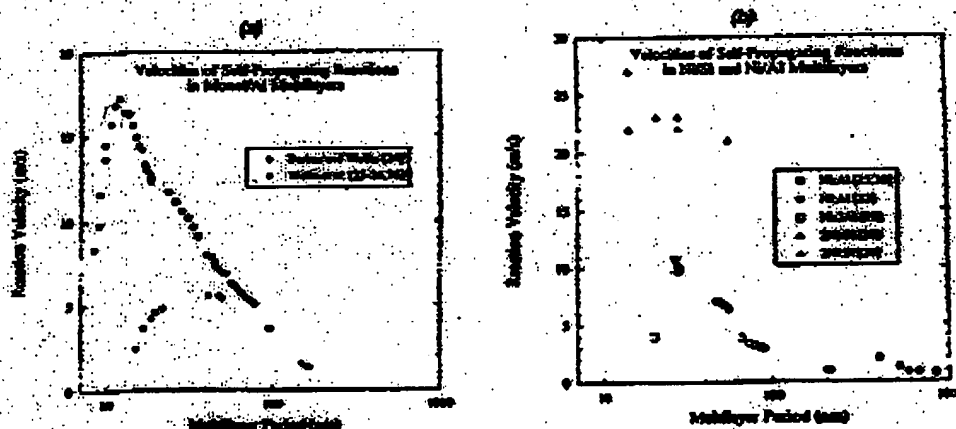


Figure F7.5. Velocities measured for self-propagating reactions in (a) Monol/AI multilayers [24-26, 38] and (b) NiSi [20] and NiAl [22, 25].

Most samples, though, begin to mix during their deposition, as shown in figures F7.2 and F7.3. This intermixing leads to heat losses and consequently a reduction in ΔH_m compared to its maximum value. We have quantified ΔH_m as a function of multilayer period for Monol/AI multilayers using differential scanning calorimetry (DSC) [25, 26, 39]. Samples with an average composition of 10Al7Ni3Cu were scanned from 50°C to 725°C, and the exothermic heat flows were integrated to yield ΔH_m [24, 25, 39]. (We also used X-ray diffraction to confirm that the product of the DSC scans, a stable B2 structure, matched the product of the self-propagating reactions.) Results for ΔH_m are plotted in figure F7.6 along with those from Barbee and Weeks [24]. Note that the driving force for the reaction clearly drops off as multilayer period decreases in both data sets. The more rapid drop off in our data set [25, 26, 39] is attributed to higher substrate temperatures and more intermixing during deposition. Note, also, that both data sets extrapolate to a similar heat at very large periods. Similar variations have been reported for heats of reaction in NiAl [37] and ZrAl [40] multilayers.

The dramatic drop in the heats of reaction for the Monol/AI multilayers in figure F7.6 substantially reduces the driving force for the self-propagating formation reactions. We believe that this reduction in driving force decreases the reaction velocities for Monol/AI samples at small periods (figure F7.5(a)). This statement

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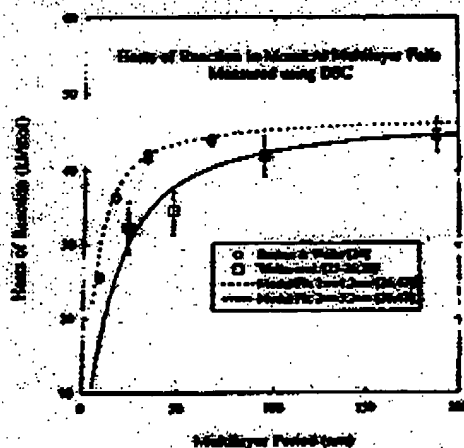


Figure F7.6. Heat of reaction for Moos/Al multilayers measured using DSC scans [24, 25]. Curves are fit to the data using equation (F.13) and $\Delta H_f = -47 \text{ kJ mol}^{-1}$.

is supported by a comparison of the two data sets in figure F7.5(a) and figure F7.6. Note that the set of samples fabricated by Barbee and Wells [24], which have higher values of ΔH_m than our samples, [25-26, 38] also have higher reaction velocities, particularly at small periods. This simple comparison suggests that intermixing between alternate layers reduces reaction velocities at small periods in some multilayer systems. To understand why intermixing does not appear to decrease reaction velocities in the Ni/Al multilayers, we must also consider reaction temperatures and intermediate transformations.

F7.3.4 Reaction Temperatures and Phase Transformations

When a reaction propagates across a multilayer sample, it should reach its maximum temperature near the trailing edge of the reaction zone, as shown in figure F7.1. We call this temperature the final temperature of the reaction, T_f , and it is determined by the heat of the reaction, ΔH_m ; the heat lost to the environment, ΔH_{loss} ; and the average heat capacity of the sample, c_p . T_f will also depend on whether or not the final product melts. If the reaction temperature exceeds the melting point of the final product, T_m , then some of its heat will be absorbed by a solid to liquid transformation of the product. To account for the endothermic effects of melting on T_f , we consider that the product could be in three different regions of solid-liquid phase space at its final temperature: it could be completely solid ($T_f < T_m$), it could be both solid and liquid ($T_f = T_m$), or it could be completely liquid ($T_f > T_m$).

In the first case where the product is completely solid ($T_f < T_m$), the enthalpy of melting (ΔH_m) can be ignored. The final temperature should be given by $T_f = (\Delta H_m + \Delta H_{loss})/(c_p M)$, where T_0 is the initial temperature and M is an average molecular mass for the sample. In the second case where the product reaches a two phase region (solid and liquid), the reaction's final temperature should be tied to the melting temperature of the product ($T_f = T_m$). In this two-phase region small variations in ΔH_m will have little impact on T_f . Moderate decreases in ΔH_m due to intermixing should reduce the amount of product that melts, but not the final reaction temperature, because T_f is tied to the melting temperature of the product. In the last case, the formation reaction has sufficient heat to melt all of the product and rise above its melting temperature. The final temperature should then be given by $T_f = (\Delta H_m + \Delta H_{loss} + \Delta H_m)/(c_p M)$ where c_p becomes an average heat capacity for the solid and liquid phases. Table F7.2 summarizes these three cases. The conditions listed in Table F7.2 predict that small changes in the heats of reactions will affect reaction temperatures when the final product is a single phase, all solid or all liquid (cases 1 and 3), but not when the product is both solid and liquid (case 2).

An example of case 1 was reported by Ma *et al* [19]. They ignited self-propagating reactions in Ni/Al

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Table F7.1. Conditions for determining final reaction temperatures.

Case	Product phase	Final reaction temperature	Conditions for final reaction temperature	Examples of multilayer systems
1	solid	$\frac{-(\Delta H_{\text{rxn}} + \Delta H_{\text{melt}})}{c_p M}$	$\frac{-(\Delta H_{\text{rxn}} + \Delta H_{\text{melt}})}{c_p M} < T_m$	Ni ₃ Al Al ₅₀ Ni ₅₀ Co ₅₀
2	solid and liquid	T_m	$\frac{-(\Delta H_{\text{rxn}} + \Delta H_{\text{melt}})}{c_p M} > T_m$ $\frac{-(\Delta H_{\text{rxn}} + \Delta H_{\text{melt}} + \Delta H_{\text{melt}})}{c_p M} < T_m$	NEAl ₃ NEAl Ni ₂ Si
3	liquid	$\frac{-(\Delta H_{\text{rxn}} + \Delta H_{\text{melt}} + \Delta H_{\text{melt}})}{c_p M}$	$\frac{-(\Delta H_{\text{rxn}} + \Delta H_{\text{melt}} + \Delta H_{\text{melt}})}{c_p M} > T_m$	PdAl PtAl

enthalpy of Ni₃Al (-38 kJ mol^{-1}) is too low to reach the compound's melting temperature (1385°C) [12-14], and since their final microstructure showed no signs of melting during the reaction [19], they concluded that the product was completely solid at T_f . In this case the reaction temperature should vary with the heat of reaction, and increasing heat decreases ΔH_{rxn} should also reduce the final reaction temperature.

Several examples for case 2 have also been reported. When reactive multilayers mix and form Ni₃Al [19], NEAl [22], or Ni₂Si [20], enough heat is generated to melt at least some of the product. With the formation of NEAl and Ni₂Si, Dyer *et al* [22] and Cleveger *et al* [20] actually measured the final temperature for each formation reaction using optical pyrometry. They found that T_f was equivalent to the melting temperature of each compound: 1638°C and 1306°C, respectively. In all three of these examples, some fraction of the reaction's heat, ΔH_{rxn} , was consumed in melting the product. Therefore, as ΔH_{rxn} drops at small periods due to intermixing, the amount of product that melts will decrease. But, the reaction's temperature remains fixed at T_m as long as some melting occurs. The temperature (and velocity) of such a reaction should have only a small dependence on ΔH_{rxn} .

So far the discussion of phase transformations has focused mainly on the formation of chemically stable compounds. However, self-sustained reactions can also produce many intermediate phases such as metastable compounds or liquid reactants. For example, Al powders often melt prior to mixing completely in powder compacts [9, 10]. Dordani and Yavari [21] suggest that a similar melting of Al occurs in Pd/Al multilayers based on thermocouple measurements. A sharp plateau at 660°C in a temperature versus time plot is a strong indication of this transformation. Additional characterizations of temperature profiles may prove useful in identifying the appearance of other intermediate phases in these rapid formation reactions.

F7.1. MODELLING SELF-PROPAGATING REACTIONS IN MULTILAYER FOILS

The foregoing results and discussion suggest that the heat, the temperature, and the transformations of a reaction impact how rapidly it propagates. The exact nature of this impact will now be explored by reviewing past [24, 41-46] and recent [26] efforts to model self-sustaining reactions in layered media. In simplest terms, the speed at which a reaction can propagate along a multilayer foil depends on how rapidly the atoms diffuse normal to the layering and how rapidly heat is conducted along the length of the foil (Figure F7.1). Most efforts to model self-propagating reactions in layered materials assume that the atomic and thermal diffusion can be treated as one-dimensional processes, occurring normal and parallel to the sample's layering. The models typically use the following governing equations for atomic diffusion:

$$\frac{\partial C}{\partial t} - \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = 0 \quad (\text{F7.1})$$

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and thermal diffusion

$$C_p \rho \frac{dT}{dt} - C_p \rho \lambda \frac{dT}{dx^2} = \frac{dQ}{dt} \quad (F7.2)$$

where C is composition, t is time, T is temperature, and Q is heat. D , λ , C_p and ρ are average values of mass diffusivity, thermal diffusivity, heat capacity, and density, and x and y lie parallel and perpendicular to the layering, as shown in figure F7.1. The atomic and thermal diffusions described by equations (F7.1) and (F7.2) can be coupled through the rate at which heat is generated, dQ/dt . Most authors assume that the rate of heat generation scales linearly with the rate at which composition changes

$$\frac{dQ}{dt} = \frac{dC}{dt} \quad (F7.3)$$

Barber and Wells [24] developed an empirical model for reaction velocities based on the above theoretical arguments and experimental observations. Their model yields accurate fits to the current data sets and has some predictive capabilities. In terms of analytical models, Armstrong [42-44] used equations (F7.1) to (F7.3) to predict reaction velocities in foils with chemically distinct layers. He assumed that heat losses to the environment are negligible and that the final temperature was constant at $T_f = T_0 + \Delta H_f / C_p M$. Reaction velocity, v_r , is then given by

$$v_r^d = \frac{D_0 \exp\left(-\frac{E}{RT_f}\right) \frac{\Delta H_f}{R}}{2 \Delta L} \quad (F7.4)$$

where $D = D_0 \exp(-E/RT)$ is the interdiffusion coefficient and 4δ is equal to the multilayer period (figure F7.1) [42-44]. This result suggests that for an ideal system with chemically distinct layers and no heat losses, the velocity of the reaction is inversely dependent on the thickness of the layers and exponentially dependent on the final temperature of the reaction. Much of the data in figure F7.5 support the $1/\delta$ dependence, particularly the NiAl data which are expected to have a constant T_f . However, Armstrong's model [42-44] fails to predict the drop-off in velocities at small multilayer periods for the MoNiAl multilayer samples. This failure stems from the fact that the individual layers in real systems are not entirely chemically distinct and intermixing will cause ΔH_f (and in some cases T_f) to vary as a function of multilayer period [24-26, 39].

To account for the loss of driving force due to intermixing, Mann *et al.* [26] generalized Armstrong's solution to include multilayer foils in which the initial composition profile is allowed to vary as $C_0(y)$ (figure F7.7(a)). Reaction velocity is then given by

$$v_r = \frac{D_0 \exp\left(-\frac{E}{RT_f}\right) \frac{\Delta H_f}{R}}{2 \Delta L} \left[\sum_{n=1}^{\infty} \frac{k_n}{\alpha_n} \right]^{-1} \quad (F7.5)$$

where T_0 is the initial temperature, T_f is the final temperature, T_{ad} is the ideal adiabatic temperature, and α_n and k_n are Fourier eigenvalues and coefficients and are calculated for each multilayer period using

$$\alpha_n = \frac{n\pi}{2\delta} \quad (F7.6)$$

and

$$k_n = \frac{1}{2\delta} \int_{-\delta}^{\delta} C_0(y) \sin(\alpha_n y) dy \quad (F7.7)$$

where n is a positive, odd integer. The final reaction temperature is also calculated but its value depends on the status of the final product and the degree of intermixing given by $C_0(y)$. For samples that remain completely solid, T_f is given by

$$T_f = T_0 + \frac{\Delta H_f}{C_p \rho N} \frac{1}{\delta} \int_{-\delta}^{\delta} C_0(y) dy \quad (F7.8)$$

where ΔH_f is the heat of formation for the final product and N is Avogadro's number. When the final product is both liquid and solid

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and when the product is completely liquid

$$T_i = T_0 - \left(\frac{\Delta H_m}{c_p \rho N} \right) - \left(\frac{\Delta H_f}{c_p \rho N} \right) \frac{1}{\delta} \int_0^\delta C_0(y) dy \quad (F7.10)$$

where ΔH_m is the enthalpy needed to melt the product at T_m . In all three cases heat losses to the environment are still ignored, and c_p , ρ , D_0 , E and λ are taken to be independent of temperature [26].

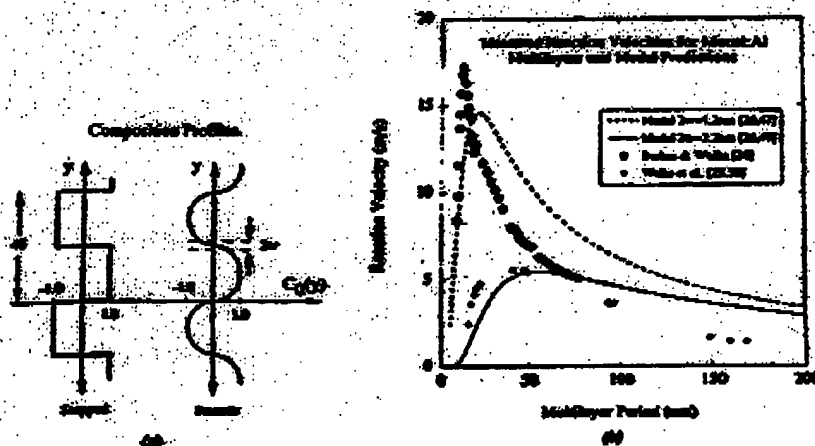


Figure F7.7. (a) Composition profiles in multilayer foil, and (b) measured and predicted reaction velocities for Mo-Ni-Al multilayers [24-26]. Velocities were predicted using equations (F7.5)-(F7.13) [26].

To predict reaction temperatures and velocities using equations (F7.5)-(F7.10), the composition profile must first be determined. Armstrong [42-44] assumed chemically distinct layers or sharp step functions for $C_0(y)$, as shown in figure F7.7(a). We considered different composition profiles [26, 47] including an exponential variation of $C_0(y)$

$$C_0(y) = 1 - \exp\left(-\frac{\ln 2}{w} y\right) \quad 0 < y \leq \delta \quad (F7.11)$$

$$C_0(y) = -1 + \exp\left(\frac{\ln 2}{w} y\right) \quad -\delta < y < 0 \quad (F7.12)$$

where $C_0(y)$ varies from 1 to -1 on going from the middle of one layer to the middle of the next (δ to $-\delta$), as shown in figure F7.7(b). With this exponential variation, $2w$ defines the thickness of the intermixed layer and we assume its composition ranges from 0.5 to -0.5. This exponential profile yields a smooth variation in composition, much like the one measured by Ma et al [31] for Ni-3Al multilayers (figure F7.3(b)).

The degree of intermixing can be quantified directly using measured composition profiles (figure F7.3(b)) or indirectly using measured heats of reaction. We used the latter approach [26, 47]. We integrated $C_0(y)$ to predict heats of reaction for Ni-Mo-Al multilayers

$$\Delta H_m = \frac{\Delta H_f}{\delta} \int_0^\delta C_0(y) dy \quad (F7.13)$$

and then fit these predictions to the measured values in figure F7.6 by varying $2w$. We found that the intermixed thickness ($2w$) was 1.2 nm in the earlier samples from Barbee and Willis [24] and 3.2 nm in our current samples [25, 26]. With a knowledge of $2w$ for the exponential profiles in equations (F7.11) and (F7.12), we then calculated reaction velocities for the two sets of Mo-Ni-Al samples using average room temperature properties and equations (F7.5)-(F7.8). Examples of the calculated velocities are plotted, along with the experimental values, in figure F7.7(b). Note that there is a clear inverse dependence of reaction

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that the drop-off occurs at larger bilayer periods in the samples with greater intermixing. This agreement between predicted and measured values suggests Mann's model predicts the general experimental trends correctly, though it must be refined further to predict absolute values accurately. Future predictions can be enhanced by accounting for heat losses to the environment, by incorporating temperature variations into the physical properties, by quantifying accurate activation energies for the atomic diffusion in these reactions, and by accounting for phase transformations of the constituents [26]. Phase transformations, such as the melting of the reactants, could be particularly important factors [21, 26], as noted early in SHS reactions [9, 10].

So far the theoretical attempts to predict the kinetics of self-propagating reactions have outpaced the corresponding experimental efforts. Besides low temperature DSC studies of formation reactions, few researchers have studied the kinetics of self-propagating reactions in nanoscale multilayers. In the first attempt to measure activation energies in reactive multilayers, Dyer *et al.* [22] fit Armstrong's analysis [42-44] (equation (E7.4)) to their velocity data for Ni/Al multilayer foils. They determined an average activation energy of 120 kJ mol^{-1} , but they did not vary reaction temperatures to confirm the exponential dependence of velocity on E . We recently tried to do so [38] by heating Moni/Al multilayer foils above 25°C prior to ignition. While we did not verify increases in the final reaction temperatures, we did find consistent increases in reaction velocities with ignition temperature, as shown in Figure E7.5. These increases suggest that the final reaction temperature also rises with T_0 . To make a crude estimate of activation energies, we assumed T_f increased directly with T_0 and performed a simple Arrhenius analysis using equation (E7.5). We plotted $\ln(V_f/T_f)$ versus $1/T_f$ and estimated that the activation energy varied from 120 kJ mol^{-1} to 196 kJ mol^{-1} as multilayer period increases from 32 nm to 194 nm. These values compare favorably with the 123 kJ mol^{-1} activation energy reported by Dyer *et al.* [22]. However, truly quantitative measurements of activation energies, and reaction kinetics in general, will require accurate measurements of final reaction temperatures.

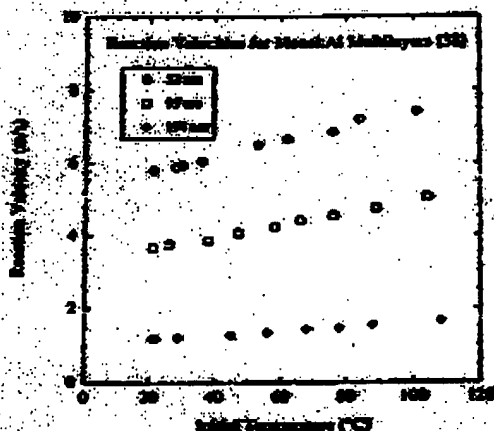


Figure E7.5: Velocities for self-propagating reactions in Moni/Al multilayers increase as the reactants are ignited at higher initial temperatures [38].

E7.5 CONCLUSIONS

We have explored a recently discovered phenomenon in nanoscale multilayer materials: self-propagating, exothermic formation reactions. The reactions are ignited with a small pulse of energy and can propagate rapidly across samples. Compared to powder compacts that are used in SHS formation reactions, multilayer samples have smaller diffusion distances for mixing and therefore can release their heats of formation more rapidly. The reactions travel much faster in multilayer samples and they are easily ignited at room temperature. Systematic investigations of the heats, the temperatures, and the velocities of these reactions

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The initial work on reactive multilayers suggests that the heat of reaction (which is produced by a reduction in atomic bond energy) can vary with multilayer period for a given set of samples. At large periods ΔH_m approaches the enthalpy of formation for a particular reaction, and at smaller periods atomic intermixing can reduce ΔH_m dramatically. This reduction in a reaction's heat can lead to a decrease in both its temperature and its velocity. The velocity at which a reaction propagates is controlled by atomic diffusion between the alternate layers and by the thermal diffusion along the layers. At large multilayer periods, the velocity is inversely dependent on multilayer period and decreases smoothly as period increases. However, at very small periods, reaction velocity can drop dramatically if the final reaction temperature is decreased by intermixing during sample fabrication. The initial experimental and theoretical reports support these conclusions. However, a much larger body of research is needed to fully establish and verify the structure-property relationships in these novel reactive materials. Successful completion of such work will speed the commercial application of reactive multilayers as local heat sources for joining and ignition technologies.

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